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STUDY 3

CHEM 041101

Ethoprop

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Feung, C.S. and D. Stillwell, III. 1995. O-ETHYL-S-PROPYL PHOSPHOROTHIOIC ACID-S-Propyl Phosphorothioic Acid (Ethoprop Metabolite) Adsorption/Desorption Study. Project Number: RPAC Study No. EC-94-291. Unpublished study performed and submitted by Rhone-Poulenc Ag Company, Research Triangle Park, NC.

REVIEWED BY:

Dana Spatz, Chemist

Environmental Risk Branch I

Environmental Fate and Effects Division/OPP

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CONCLUSIONS:

Aged (Degradate) Mobility - Leaching and Adsorption/Desorption

- 1. This study is <u>acceptable</u> and may be used towards the fulfillment of the Leaching-Adsorption/Desorption data requirement.
- 2. The adsorption/desorption of O-ethyl-S-propyl phosphorothioic acid-S-propyl phosphorothioic acid, the M1 metabolite of ethoprop, was studied in four soils and a pond sediment. Freundlich adsorption values were 0.525 in a silt loam, 0.505 in a sandy loam, 0.527 in a loamy sand, 1.24 in a pond sediment, and 4.12 in a clay soil. Koc values were 129, 109, 43, 50, and 1652, respectively. O-ethyl-S-propyl phosphorothioic acid is considered to be very highly mobile in all the tested soils, except for the clay where it was less mobile. Desorption data showed that the desorption constants ranged from 1.0 to 11.4 (1st desorption), from 4.9 to 36.7 (2nd desorption), and from 37.7 to 526 (3rd desorption). Binding appeared to increase with successive desorption cycles.

METHODOLOGY:

Silt loam, sandy loam, loamy sand, pond sediment and clay soils were sieved (2 mm). [¹⁴C] O-ethyl-S-propyl phosphorothioic acid-S-propyl phosphorothioic acid (specific activity: 48,985 dpm/ug, >99% radiochemical purity) was used as the dosing solution. Approximately 5 grams of soil or sediment was added to each of 40 Pyrex centrifuge tubes (duplicate tubes x 4 concentrations x five soil/sediment types). Four tubes were

used as blanks without soil to determine if any [14 C] O-ethyl-S-propyl phosphorothioic acid-S-propyl phosphorothioic acid was adsorbed by the centrifuge tube and screw cap. 25 ml of 0.01 M CaCl₂ solution containing one of the four concentrations of O-ethyl-S-propyl phosphorothioic acid-S-propyl phosphorothioic acid (final water concentrations were 0.043, 0.415, 2.057, and 4.067 ppm) was added to each tube and shaken for 3 hours in the dark at 26 ± 1 °C (the clay soil samples were shaken for 8 hours based on the preliminary studies). After equilibrium was achieved, the tubes were centrifuged for 3 minutes at 2500 rpm. The supernatant was decanted and analyzed by LSC.

To determine desorption, the supernatant was replaced with pesticide-free 0.01 M CaCl₂ solution and the soil:solution slurries were shaken for 3 hours in the dark (the clay soil samples were shaken for 24 hours). After the desorption period, the slurries were centrifuged and the supernatant was decanted. Aliquots of the supernatant were analyzed by LSC. This procedure was repeated two additional times.

Following the final desorption, the soil residues were allowed to air dry and were combusted.

Aliquots of the adsorption supernatants were analyzed by 2-D TLC. Silica gel plates were developed in the following systems: a) acetonitrile/water, 80/20 (v/v), b) acetonitrile/ethanol/water, 60/20/20 (v/v/v), and c) ethanol/water, 70/30 (v/v). Solvent system "a" or "b" was used for the first dimensional direction and solvent "c" for the second direction.

DATA SUMMARY:

Based on batch equilibrium experiments, [14 C] O-ethyl-S-propyl phosphorothioic acid-S-propyl phosphorothioic acid at nominal concentrations of 0.043, 0.415, 2.057, and 4.067 ppm, showed very high mobility in silt loam, sandy loam, pond sediment, and loamy sand soil:solution slurries equilibrated for 3 hours at $26 \pm 1^{\circ}$ C. Mobility was less in a clay soil:solution slurry equilibrated for 8 hours. Freundlich K_{ads} values were 0.525 for silt loam soil, 0.505 for sandy loam soil, 0.527 for loamy sand soil, 1.24 for pond sediment, and 4.12 for clay soil; respective K_{∞} values were 129, 109, 43, 50, and 1652.

Freundlich K_{des} values (desorption cycle 1) were 1.0 for the silt loam soil, 1.1 for the sandy loam soil, 1.4 for the loamy sand soil, 1.7 for the pond sediment, and 11.4 for the clay soil. All the soils showed increasing values of K_{des} between the first, second, and third cycles, indicating increased binding to soils during the desorption cycles.



The material balances for the definitive study ranged from 95.4-101.55% for the sandy loam, 95.15-98.51% for the loamy sand, 95.06-99.78% for the silt loam, 50.45-76.80% for the clay and 66.80-96.89% for the pond sediment.

COMMENTS:

- 1. 1/n values for adsorption ranged from 0.979 for the sandy loam, to 0.569 for the pond sediment.
- 2. The results of 2-D TLC analysis of the supernatant showed that the test substance was fairly stable during adsorption.

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